Examining Growth Rates of Iron Oxide Heterogeneous Phase Transformations

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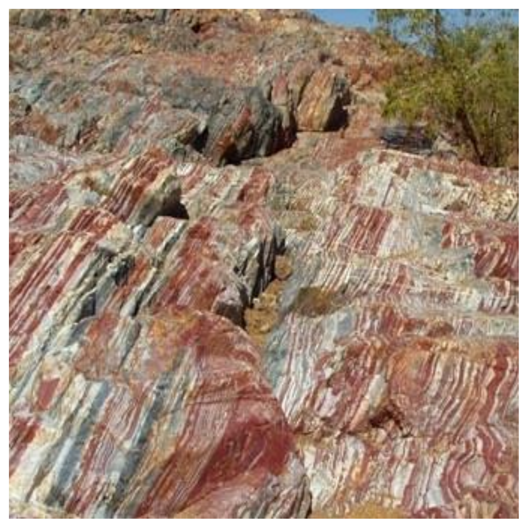
Introduction

In natural environments, dissolved iron species can undergo oxidation-reduction reactions to precipitate as the iron oxide mineral ferrihydrite. Due to thermodynamic instability of ferrihydrite crystals, they may undergo mineral phase transformation into goethite and hematite. This process is pH- and temperature-dependent and may be accelerated in the laboratory setting.

Ferrihydrite

Goethite



Hematite

Mineral phase transformations and particle growth are thought to occur along two major mechanisms: dissolution precipitation (DP) and interface nucleation (IN). In DP, larger crystals grow at the expense of smaller crystals as dissolved mineral species re-precipitate onto other structures. In IN, a new mineral phase nucleates at the interface formed by the contact of two nanoparticle surfaces. The equation for the IN model is showed in Equation 1, while a combined IN-DP model is described in Equation 2.

$$\ln\left[\frac{1}{(1-a)(1)^3} - 1\right] = \ln[k_{in}N_0] + lnt \qquad (1)$$

$$\ln\left[\frac{k_{dp}}{(1-a)}(1)^3 + k_{in}N_0\right] = k_{dp}t + \ln\left(k_{dp} + k_{in}N_0\right) \qquad (2)$$

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Materials and Methods

6-line ferrihydrite, goethite, and hematite were synthesized and adjusted to pH 5. Samples of ferrihydrite and were spiked with goethite and hematite to make the ratios: 0% goethite/0% hematite (Fh), 4% goethite/0% hematite (4Gt), 4% goethite/3.5% hematite (4Gt/3.5Ht), and 0% goethite/3.5% hematite (3.5Ht)

Samples were aged in a 90°C oven and taken out at various timepoints over a course of 6 days. After aging, the samples were dried and ground with pestle and mortar for analysis via X-ray diffraction (XRD).

Determining Phase Transformations Using XRD

XRD analysis indicate that samples initially spiked with goethite were able to initiate goethite formation from 6-line ferrihydrite more rapidly then samples without initial goethite "seed crystals". Our results using the kinetic growth models showed that the IN growth mechanism dominated the Fh sample, along with the samples containing hematite (3.5Ht, 4Gt/3.5Ht). 4Gt had the least IN influence and DP influenced phase transformation after 60 hours of aging. When compared to each other, 4Gt/3.5Ht had more DP character than 3.5Ht. Overall, our results show that the phase transformations for iron oxides are dominated by the interface nucleation mechanism.

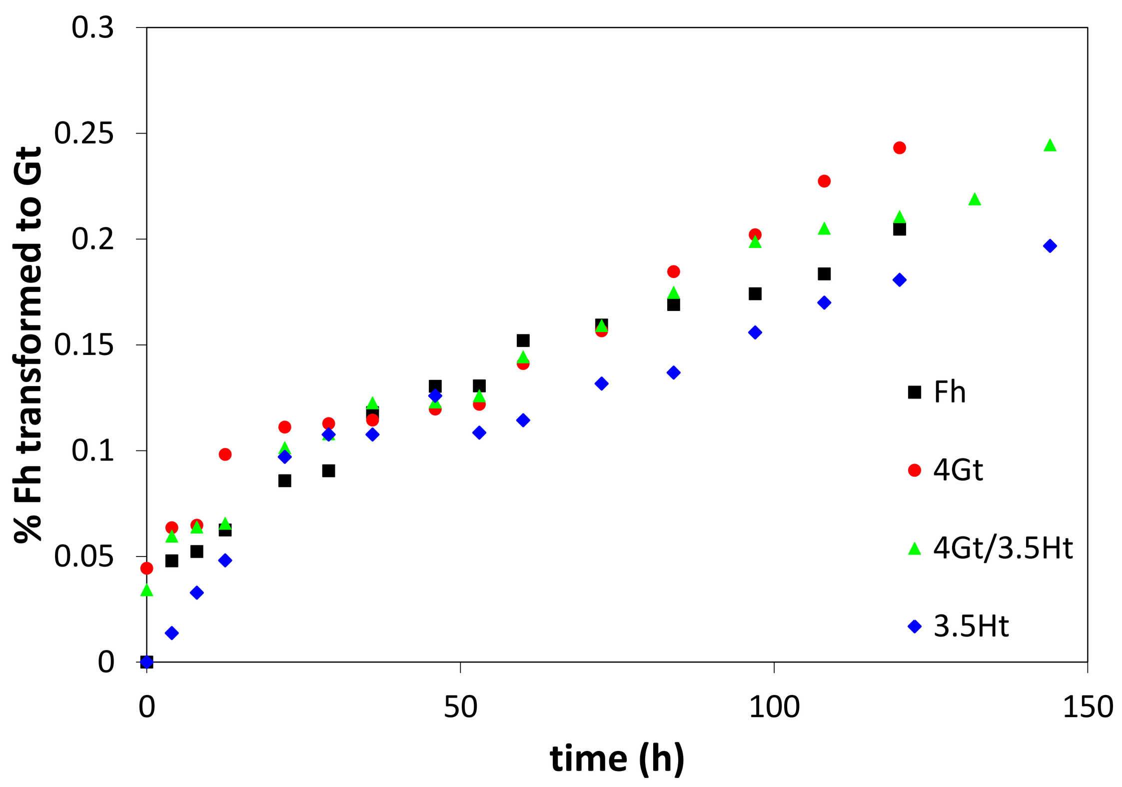

Figure 1. Overall ferrihydrite (Fh) conversion to goethite (Gt) in each sample.

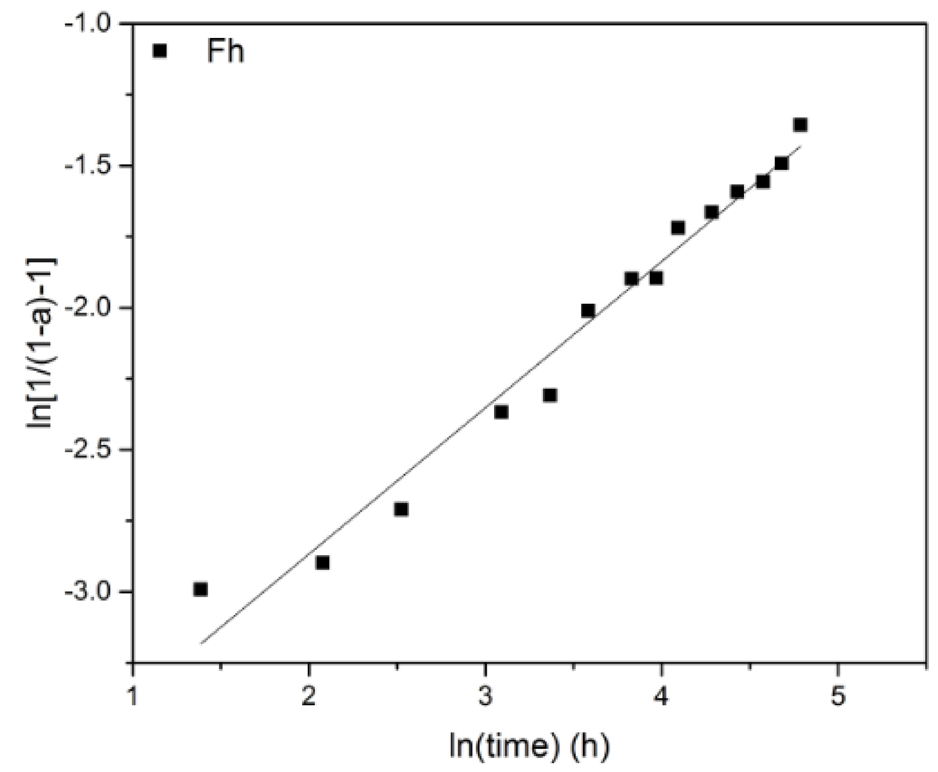

Figure 3. Fh sample using the interface nucleation (IN) model.

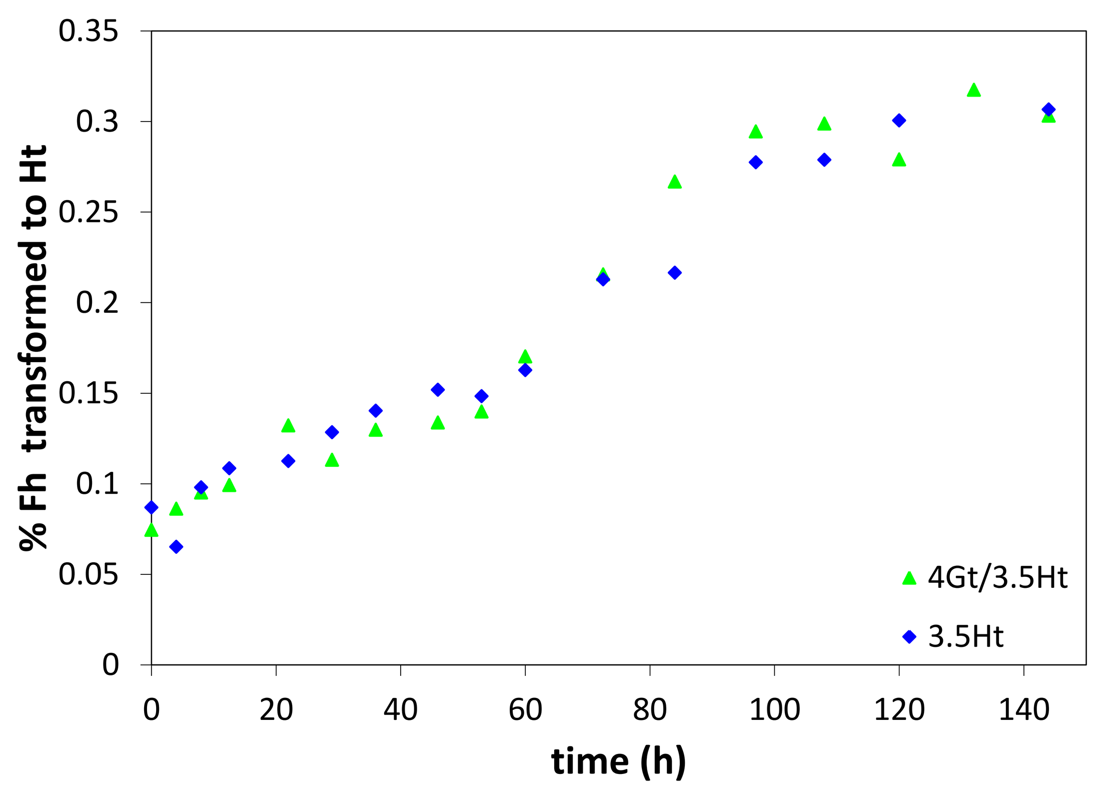

Figure 2. Overall ferrihydrite (Fh) conversion to hematite (Ht) for samples initially spiked with Ht.

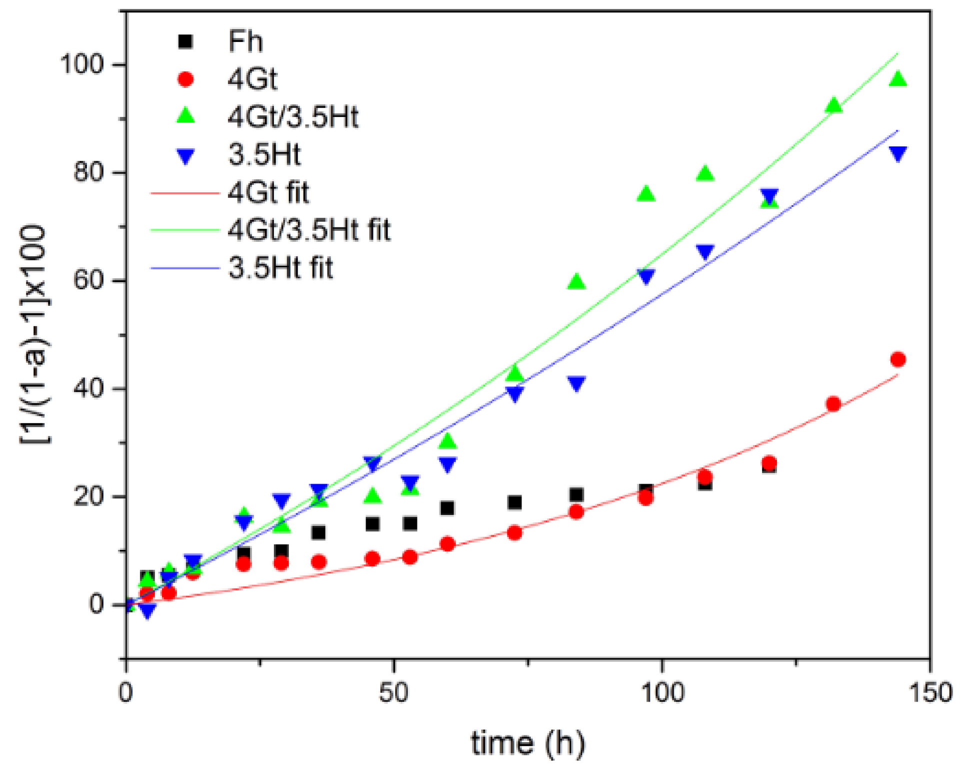

Figure 4. Results of each sample using the combined model (CM).

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